

SPECIFICATION AMENDMENTS

On page 1, above line 1, insert--Field of the Invention--

Paragraph at line 1 of page 1 has been amended as follows:

-- The present invention relates to a method for the preparation of lower ~~olefins~~ olefins by steam cracking of heavy hydrocarbons obtained by Fischer-Tropsch synthesis in a naphtha designed steam cracking furnace.--

On page 1, above line 5, insert--Background of the Invention--

On page 1, before line 9, insert--Summary of the Invention--

Paragraph at line 9 of page 1, ending at line 6 of page 2, has been amended as follows:

-- The present invention relates to the use of such heavy Fischer-Tropsch hydrocarbons for the preparation of lower ~~olefins~~ olefins. For such preparation, according to the invention, use is made of a new or available steam cracking furnace that is designed for steam cracking of a naphtha feed. Furnaces which are designed for a petroleum derived naphtha feed cannot be used for a more heavy petroleum derived feed because such a more heavy feed will not fully evaporate in the pre-heating sections of the furnace resulting in excessive coke formation in especially the superheating section of the pre-heater. Although naphtha and Fischer-Tropsch heavy hydrocarbons have different compositions, and different boiling point ranges, a naphtha designed steam cracking furnace ~~turned out to be~~ is suitable for steam cracking the more heavy Fischer-Tropsch hydrocarbons. Accordingly, these heavy Fischer-Tropsch hydrocarbons may be used according to the invention for the preparation of lower ~~olefins~~ olefins by steam cracking. Due to the difference in composition of the heavy Fischer-Tropsch hydrocarbons in comparison to naphtha, the lower ~~olefins~~ olefins produced by steam cracking comprise less aromatic compounds and thus for producing the same amount of lower ~~olefins~~ olefins less feed is required. In addition, relative to steam cracking of naphtha, steam cracking of Fischer-Tropsch heavy hydrocarbons ~~resulted~~ results in an increased production of ethene, propene, butene and a lower production of hydrogen, methane and carbon monoxide.--

On page 2, above line 7, insert--Detailed Description of the Invention--

Paragraph at line 7 of page 2 has been amended as follows:

-- --Accordingly, the present invention provides a method for the preparation of lower ~~olefines~~ olefins ethene, propene and butene by steam cracking, wherein the feed ~~comprises~~ comprising heavy hydrocarbons obtained by Fischer-Tropsch synthesis, which Fischer-Tropsch hydrocarbons have an initial boiling point of above 150°C and a final boiling point of below 400°C, is are subjected to steam cracking in a naphtha designed steam cracking furnace for steam cracking the Fischer-Tropsch hydrocarbons into the lower ~~olefines~~ olefins. ~~wherein the furnace--~~

Paragraph at line 17 of page 2 has been amended as follows:

-- Preferably, the steam cracking of Fischer-Tropsch heavy hydrocarbons is carried out in a conventional naphtha designed steam cracking furnace ~~comprises~~ comprising a convection zone provided with a first preheating zone in which the Fischer-Tropsch feed is heated, a second preheating zone in which the heated Fischer-Tropsch hydrocarbons are heated in the presence of steam to form a mixture of liquid and gaseous Fischer-Tropsch hydrocarbons; and a super heating zone in which the liquid and gaseous Fischer-Tropsch hydrocarbons are super heated; and a cracking zone in which the gaseous super heated Fischer-Tropsch hydrocarbons are steam cracked into the lower ~~olefines~~ olefins ethene, propene and butene.--

Paragraph at line 1 of page 2a has been amended as follows:

-- The initial and final boiling point of naphtha are lower than the initial and final boiling point of the heavy Fischer-Tropsch hydrocarbons, therefore. ~~This may have as an effect that the feed to the second preheating zone is~~ may not be only a gas but is may still be a mixture of gas and liquid.--

Paragraph at line 20 of page 3 has been amended as follows:

-- Generally, these Fischer-Tropsch heavy hydrocarbons comprise more than 75 wt.% n-paraffins ~~n-paraffines more than 75 wt.%~~ and preferably more than 80 wt.%. These ~~n-paraffines~~ n-paraffins generally have ~~generally~~ a carbon number of 5-25, preferably of 7-23, more preferably of 10-20.--

Paragraph at line 25 of page 3, ending at line 2 of page 4 has been amended as follows:

■ --The Fischer-Tropsch hydrocarbons to be used as a feed according to the invention may be directly obtained by the Fischer-Tropsch synthesis or indirectly after further treatment. Such a treatment may comprise fractional distillation of hydrocarbons originating from the Fischer-Tropsch synthesis. Such fractional distillation may be carried ~~carries~~ out at temperatures of 100-380 °C, preferably at 150-370 °C, and more preferably at 200-360 °C. Another ~~An other~~ pretreatment comprises hydro cracking or thermal cracking of Fischer-Tropsch hydrocarbons, ~~or by thermal cracking of Fischer-Tropsch hydrocarbons,~~ which hydro cracking or thermal cracking provides ~~provide~~ the heavy Fischer-Tropsch hydrocarbons as described above.--

Paragraph at line 3 of page 4 has been amended as follows:

-- ~~It is a preferred characteristic of the~~ Preferably, the heavy Fischer-Tropsch hydrocarbons that they are essentially free of aromatic compounds, nitrogen comprising compounds and sulfur ~~sulphur~~ comprising compounds.--

Paragraph at line 15 of page 4 has been amended as follows:

-- The hydrocarbonaceous feed suitably is methane, natural gas, associated gas or a mixture of C₁₋₄ hydrocarbons. The feed comprises mainly, i.e. that is, more than 90 v/v%, especially more than 94%, C₁₋₄ hydrocarbons, especially comprises at least 60 v/v percent methane, preferably at least 75 percent, more preferably 90 percent. Very suitably, natural gas or associated gas is used. Suitably, any sulfur ~~sulphur~~ in the feedstock is removed.--

Paragraph at line 24 of page 4 has been amended as follows:

--The partial oxidation of this hydrocarbonaceous ~~hydrocarbons~~ feed, producing mixtures of especially carbon monoxide and hydrogen, can take place according to various established processes. These processes include the Shell Gasification Process. A comprehensive survey of this process can be found in the Oil and Gas Journal, September 6, 1971, pp 86-90.--

Paragraph at line 6 of page 5 has been amended as follows:

-- To adjust the H₂/CO ratio in the syngas, carbon dioxide and/or steam may be introduced into the partial oxidation process. Preferably up to 15% volume based on the amount of syngas, preferably up to 8% volume, more ~~preferably~~ ~~preferable~~ up to 4% volume, of either carbon dioxide or steam is added to the feed. Water produced in the hydrocarbon synthesis may be used to generate the steam. As a suitable carbon dioxide source, carbon dioxide from the effluent gasses of the expanding/combustion step may be used. The H₂/CO ratio of the syngas is suitably between 1.5 and 2.3, preferably between 1.8 and 2.1. If desired, (small) additional amounts of hydrogen may be made by steam methane reforming, preferably in combination with the water shift reaction. Any carbon monoxide and carbon dioxide produced together with the hydrogen may be used in the hydrocarbon synthesis reaction or recycled to increase the carbon efficiency. Additional hydrogen manufacture may be an option.--

Paragraph at line 1 of page 6 has been amended as follows:

-- The catalysts used ~~in~~ for the catalytic conversion of the mixture comprising hydrogen and carbon monoxide are known in the art and are usually referred to as Fischer-Tropsch catalysts. Catalysts for use in the Fischer-Tropsch hydrocarbon synthesis process frequently comprise, as the catalytically active component, a metal from Group VIII of the Periodic Table of Elements. Particular catalytically active metals include ruthenium, iron, cobalt and nickel. Cobalt is a preferred catalytically active metal.--

Paragraph at line 22 of page 6 has been amended as follows:

--If desired, the catalyst may also comprise one or more metals or metal oxides as promoters. Suitable metal oxide promoters may be selected from Groups IIA, IIIB, IVB, VB and VIB of the Periodic Table of Elements, or the actinides and lanthanides. In particular, oxides of magnesium, calcium, strontium, barium, scandium, yttrium, lanthanum, cerium, titanium, zirconium, hafnium, thorium, uranium, vanadium, chromium and manganese are most suitable promoters. Particularly preferred metal oxide promoters for the catalyst used to prepare the hydrocarbons ~~waxes~~ for use in the present invention are manganese and zirconium oxide. Suitable metal promoters may be selected from Groups VIIB or VIII of the Periodic Table. Rhenium and Group VIII noble metals are particularly

suitable, with platinum and palladium being especially preferred. The amount of promoter present in the catalyst is suitably in the range of from 0.01 to 100 pbw, preferably 0.1 to 40, more preferably 1 to 20 pbw, per 100 pbw of carrier. --

Paragraph at line 5 of page 7 has been amended as follows:

-- The catalytically active metal and the promoter, if present, may be deposited on the carrier material by any suitable treatment, such as impregnation, kneading and extrusion. After deposition of the metal and, if appropriate, the promoter on the carrier material, the loaded carrier is typically subjected to calcination at a temperature of generally from 350°C to 750°C, preferably a temperature in the range of from 450°C to 550°C. The effect of the calcination treatment is to remove crystal water, to decompose volatile decomposition products and to convert organic and inorganic compounds to their respective oxides. After calcination, the resulting catalyst may be activated by contacting the catalyst with hydrogen or a hydrogen-containing gas, typically at temperatures of about 200°C to 350°C.--

Paragraph at line 20 of page 7 has been amended as follows:

-- The catalytic conversion process may be performed under conventional synthesis conditions known in the art. Typically, the catalytic conversion may be effected at a temperature in the range of from 100°C to 600°C, preferably from 150°C to 350°C, more preferably from 180°C to 270°C. Typical total pressures for the catalytic conversion process are in the range of from 1 to 200 bar absolute, more preferably from 10 to 70 bar absolute. In the catalytic conversion process mainly (at least 70 wt%), preferably 90 wt% of C₅+ hydrocarbons are formed.--

Paragraph at line 30 of page 7, ending at line 10 of page 8, has been amended as follows:

-- Preferably, a Fischer-Tropsch catalyst is used, which yields substantial quantities of normal (and also iso-) paraffins, more preferably substantially normal paraffins. A part may boil above the boiling point range of heavy hydrocarbons to normally solid hydrocarbons. A most suitable catalyst for this purpose is a cobalt-containing Fischer-Tropsch catalyst. The term heavy hydrocarbons as used herein, is a reference to hydrocarbon mixtures of which the boiling point range corresponds substantially to that of kerosene and gas oil fractions obtained in a conventional atmospheric distillation of crude

mineral oil. The boiling point range of these heavy hydrocarbons (also called middle distillates) generally lies within the range of about 100-380°C, preferably 200-370°C, more preferably 150-360°C.

Paragraph at line 11 of page 8 has been amended as follows:

-- The Fischer-Tropsch hydrocarbons generally comprise C₄-C₁₀₀, preferably C₄-C₅₀ hydrocarbons. Normally liquid Fischer-Tropsch hydrocarbons are suitably C₅-₂₅ hydrocarbons, especially C₇-₂₃ hydrocarbons, more especially C₁₀-₂₀ hydrocarbons, or mixtures thereof. These hydrocarbons or mixtures thereof are liquid at temperatures between 5°C and 30°C (1 bar), especially at about 20 °C (1 bar), and usually are paraffinic ~~in of~~ nature, while up to 24 wt%, preferably up to 12 wt%, of either ~~olefines~~ olefins or oxygenated compounds may be present. Depending on the catalyst and the process conditions used in the Fischer Tropsch reaction, normally gaseous hydrocarbons, normally liquid hydrocarbons and optionally normally solid hydrocarbons are obtained. It is preferred to obtain a large fraction of normally solid hydrocarbons. These solid hydrocarbons may be obtained up to 85 wt % based on total hydrocarbons, usually between 50 and 75 wt %.--

Paragraph at line 29 of page 9 has been amended as follows:

-- The production of lower ~~olefines~~ olefins, in particular ethene and propene, is in general achieved by pyrolyzing the heavy Fischer-Tropsch hydrocarbons. --

Paragraph at line 8 of page 10 has been amended as follows:

--Naphtha furnaces designed for treating a naphtha feed will have a larger heat transfer surface area in the first preheating zone than furnaces designed for light feed, as a heavy feed will have a higher initial boiling point than light feed and the main aim of the first preheating zone is vaporizing ~~vaporizing the feed~~ and heating the feed.--

Paragraph at line 14 of page 10 has been amended as follows:

-- A furnace designed for treating gaseous feed, will have a smaller heat transfer surface area in the first preheating zone than a furnace designed for liquid feed, as a gaseous feed does not need to be vaporized ~~vaporized~~. It is to be understood that the

scope of the steam cracking process may include any number and ~~type~~ types of process steps between each described process step or between a described source and destination within a process step.--

Paragraph at line 22 of page 10 has been amended as follows:

-- Usually and preferably, all of the product of a process step will be subjected to the next process step. However, it is possible to send only part of the product of a process step to the next process step.--

Paragraph at line 26 of page 10 has been amended as follows:

--Feed may ~~can~~ be introduced into the process at further inlets other than ~~besides~~ the standard inlet and the inlet where feed is introduced together with steam and/or dilution gas. However, it is preferred to introduce feed only at the standard inlet of the convection zone and further feed together with steam and/or dilution gas.--

Paragraph at line 32 of page 10 has been amended as follows:

--Dilution gas may ~~can~~ be added at a single inlet, or may ~~can~~ be added via several inlets. However, it is preferred to add dilution gas at a single inlet.--

Paragraph at line 3 of page 11 has been amended as follows:

--The initial boiling point of naphtha ~~can~~ may be ~~of~~ from 0°C to 100°C while final boiling points ~~can~~ may range ~~of~~ from 90°C to 250°C. The initial and final boiling points ranges of the Fischer-Tropsch hydrocarbons are shifted to higher temperatures.--

Paragraph at line 8 of page 11 has been amended as follows:

--The convection zone generally comprises a first preheating zone and a second preheating zone between which is located an inlet for steam and optionally dilution gas. In the first preheating zone, the feed is heated. After the first preheating zone, steam and optionally dilution gas is added to the feed and the mixture obtained ~~can~~ may be heated further in the second preheating zone to a temperature just below the temperature at which cracking starts to occur. The temperature of the product obtained from the convection zone will usually be ~~of~~ from 400°C to 800°C, depending upon the feed, more specifically ~~of~~ from 450°C to 750°C.--

Paragraph at line 20 of page 11, ending at line 6 of page 12, has been amended as follows:

--The pyrolysis furnace may be any type of conventional ~~olefines~~ olefins pyrolysis furnace designed for pyrolyzing heavy feed and operated for production of lower boiling products such as ~~olefines~~ olefins, especially including a tubular steam cracking furnace. The tubes within the convection zone of the pyrolysis furnace may be arranged as a bank of tubes in parallel, or the tubes may be arranged for a single pass of the feedstock through the convection zone. Within each bank, the tubes may be arranged in a coil or serpentine type arrangement. At the inlet, the feed may be split among several tubes, or may be fed to one single pass tube through which all the feed flows from the inlet to the outlet of the first stage preheater. Preferably, the first and/or second preheating zone of the convection zone comprise a multiple pass tubular reactor in which feed is passed through the first and/or the second preheating zone via more than one tube. Multiple pass tubular reactors often contain tubes having connections at their ends leading feed from the one tube to the next tube until the feed is sufficiently heated to be mixed with dilution gas and be passed to the second preheating zone, or to be sent to the cracking zone.--

Paragraph at line 7 of page 12 has been amended as follows:

--The pressure and temperature at which the feed is fed to the inlet of the first preheating zone is not critical, typically the temperature will be ~~ef~~from 0°C to 300°C.--

Paragraph at line 26 of page 12 has been amended as follows:

-- The heating elements in the first and second preheating zone in the convection zone is typically a bank of tubes, wherein the contents in the tubes are heated primarily by convective heat transfer from the combustion gas exiting from the cracking zone of the pyrolysis furnace, so-called flue gas. However, different heating elements may ~~can~~ be used as well.--

Paragraph at line 33 of page 12, ending at line 2 of page 13, has been amended as follows:

-- The pressure within the first and second preheating zone is not particularly limited. The pressure is generally within a range of from 4 to 21 bar, more preferably ~~ef~~from 5 to 13 bar.--

Paragraph at line 3 of page 13 has been amended as follows:

--In the process of the present invention, part of the heavy hydrocarbon feed ~~hydrocarbons~~ obtained by Fischer-Tropsch synthesis ~~as the feed is~~ may be introduced via the standard feed inlet of the convection zone, and if desired, part of the feed is may be introduced further downstream in the convection zone.--

Paragraph at line 13 of page 13 has been amended as follows:

--The dilution gas is a vapor ~~vapour~~ at the injection point into the convection zone. Examples of dilution gases are methane, ethane, nitrogen, hydrogen, natural gas, dry gas, refinery off gases, and a vaporized ~~vapourized~~ naphtha. Preferably, the steam is superheated steam.--

Paragraph at line 18 of page 13 has been amended as follows:

-- Typical dilution gas temperatures at the dilution gas/feed junction range of from 140°C to 800°C, more preferably of from 150°C to 780°C, more preferably of from 200°C to 750°C.--

Paragraph at line 22 of page 13 has been amended as follows:

--The pressure of dilution gas is not particularly limited, but is preferably sufficient to allow injection. Typical dilution gas pressures added to the feed ~~crude oil~~ is generally ~~within the range of~~ from 6 to 15 bar.--

Paragraph at line 26 of page 13 has been amended as follows:

-- It is desirable to add steam and optionally dilution gas between the first preheating zone and the second preheating zone in an amount which will generally ~~be~~ not be more than 1 kg of dilution gas per kg of feed. However, there may ~~can~~ be circumstances in which a higher amount of dilution gas may ~~can~~ be advantageous.--

Paragraph at line 9 of page 14 has been amended as follows:

-- Subsequently, the product of the convection zone is sent to the cracking zone. The temperature of the mixture of steam and feed is increased further under controlled residence time, temperature profile and partial pressure. The exit temperature of the

product obtained in the cracking zone is generally ~~of~~ from 700°C to up to 1000°C.
more specifically of from 750°C to 950°C. The pressure is generally within a range of
from 2 bar to 25 bar, more preferably of from 3 bar to 18 bar.--

Paragraph at line 21 of page 14 has been amended as follows:

-- On leaving the cracking zone, the products are generally immediately cooled.
The temperature of the product will usually be reduced to a temperature of from 200°C to
700°C, more specifically ~~of~~ from 250°C to 650°C to prevent degradation by secondary
reactions. Cooling of the product obtained in the cracking zone may ~~can~~ be done in any way
suitable, such as by direct quenching or indirect quenching.--

Paragraph at line 29 of page 14, ending at line 2 of page 15, has been amended as follows:

-- The cooled product is subsequently separated into the desired end-products.
Separation of the desired end-products may ~~can~~ start at cooling where heavy components
can be removed. Further, during cooling, the gas obtained may ~~can~~ be compressed, and
acids and water ~~can~~ be removed. Subsequently, the product may ~~can~~ be dried, and
uncracked feed, ethane and propane may be recovered for recycling as pyrolysis feed. The
cracking severity affects the composition of the product obtained. --

Paragraph at line 3 of page 15 has been amended as follows:

-- Products of an ~~olefines~~ olefins pyrolysis furnace include, but are not limited
to, ethene, propene, butadiene, benzene, hydrogen, and methane, and other associated
olefinic, paraffinic, and aromatic products. Ethene generally is the predominant product,
typically ranging from 15 to 60 %wt, based on the weight of the feed.--

Paragraph at line 9 of page 15 has been amended as follows:

-- In a typical work-up, the product of the cracking zone is cooled with the help
of a water quench, followed by multi-stage compression typically in 4 to 6 stages. Before
the last compressor stage, the gas may be ~~is~~ treated with caustic to remove hydrogen
sulphide ~~sulphide~~ and carbon dioxide. Actetylenes may be hydrogenated with hydrogen-
rich compressor gas. After the last compression stage, the cracked gas is typically
dehydrated by chilling and dried by use of molecular sieves. Methane and hydrogen may
~~can~~ be removed in a demethanizer. In a demethanizer, the hydrocarbons containing 2

carbon atoms are produced overhead and the hydrocarbons containing 3 carbon atoms or more are is a bottom product. The overhead stream may ~~can~~ be hydrogenated to remove acetylene and then fractionated to produce ethene and ethane. The ethane may ~~can~~ be recycled. The bottom product may ~~can~~ be further fractionated, if appropriate, to remove heavy ends including compounds containing 4 carbon atoms or more. The overhead stream from a depropanizer may ~~can~~ be hydrogenated to remove methylacetylene and propadiene, which can be recovered for sale or removed via other means. Propene may ~~can~~ be obtained as overhead stream from the depropanizer, and the bottom propane fraction may ~~can~~ be recycled.--

Paragraph at line 32 of page 15, ending at line 2 of page 16, has been amended as follows:

--Any percentage mentioned in this description is calculated on total weight or volume of the composition, unless indicated otherwise differently. When not mentioned, percentages are considered to be weight percentages. Pressures are indicated in bar absolute, unless otherwise indicated ~~differently~~.--

On page 17, above line 1, insert --We claim:--